

REMARKS

Applicants have amended their claims in order to further clarify the definition of various aspects of the present invention. In particular, all previously considered/presented claims have been cancelled without prejudice or disclaimer, and by the present amendments Applicant is adding new claims 33-42 to the application. All of these newly added claims are directed to a method of manufacturing a semiconductor integrated circuit device, with claim 33 being the sole newly added independent claim. Claim 33 recites that this method includes steps of providing a silicon wafer covered with an insulating film whose main surface is mainly formed of silicon oxide; cleaning a surface of the silicon wafer covered with the insulating film whose main surface is mainly formed of silicon oxide, by a sheet-by-sheet manner at an ordinary temperature, with use of a processing solution which contains hydrogen peroxide, hydricid fluoride salt and water, and also contains HF and HF_2^- as etching seeds of the silicon oxide, under conditions that the insulating film is etched but the silicon wafer is not etched, the concentration of the hydricid fluoride salt being set forth; removing the insulating film after the cleaning step, by applying a processing solution which includes hydricid fluoride and water, to expose the surface of the silicon wafer; drying the wafer after removing the insulating film; and subjecting the wafer to a heat treatment after drying the wafer, to form a gate oxide film over the wafer. Claims 34 and 35, each dependent on claim 33, respectively further define the hydricid fluoride salt; and claim 36, also dependent on claim 33, recites that the processing solution further includes a surfactant. Claims 37 and 38, each dependent on claim 33, respectively recites that during the cleaning step the processing solution is ultrasonically vibrated; and recites that the heat-treatment step (e) is performed after the drying step

without contacting the silicon wafer with the air. Claims 39 and 40, each dependent on claim 33, respectively recites a temperature of the processing solution during the processing, and recites a pH of the processing solution; and claims 41 and 42, each dependent on claim 33, respectively further defines the heat treatment in step (e), and recites that the silicon wafer is transferred to a chamber immediately after the drying step (d) to perform the heat treatment of step (e), to form the gate oxide film.

In connection with these newly added claims, note, for example, pages 14-18 of Applicant's specification. Note also the first full paragraph on page 23 thereof.

Applicant respectfully submits that all of the claims now presented for consideration by the Examiner patentably distinguish over the teachings of the references applied by the Examiner in the Office Action mailed June 4, 2003, that is, the teachings of the U.S. Patents to Ohmi, et al., No. 5,990,060 (Ohmi '060), to Wang, No. 6,087,243, to Okutani, No. 5,135,608, and to Ohmi, et al., No. 5,277,835 (Ohmi '835), and the pertinent pages of the publication by Wolf, et al., Silicon Processing for the VLSI Era, Vol. 1: Process Technology (1986), pages 198 and 201, under the provisions of 35 USC §103.

It is respectfully submitted that these references as applied by the Examiner would have neither taught nor would have suggested such a method of manufacturing a semiconductor integrated circuit device as in the present claims, including, inter alia, cleaning the surface of the silicon wafer covered with an insulating film whose main surface is mainly formed of silicon oxide, by a sheet-by-sheet manner, with the cleaning being performed at an ordinary temperature with use of a processing solution which contains hydrogen peroxide, hydric acid fluoride salt and water, and also contains HF and HF₂⁻ as etching seeds of the silicon oxide, under conditions that the insulating film is

etched but the silicon wafer is not etched, the concentration of the hydracid fluoride salt in the processing solution being in a range of about 0.1 to 3 mol/l; and with the insulating film then being removed to expose the surface of the silicon wafer and the silicon wafer then being dried and then subjected to a heat treatment to form a gate oxide film over the silicon wafer. See claim 33.

In particular, and as will be shown infra, it is respectfully submitted that the teachings of the applied references do not disclose the claimed method, including the cleaning step using the recited processing solution having the recited etching seeds, and under conditions that the insulating film is etched but the silicon wafer is not etched, as in the method of claim 33.

In addition, it is respectfully submitted that the teachings of the applied prior art would have neither disclosed nor would have suggested such aspects of the present invention as in the remaining, dependent claims, having features as in claim 33 as discussed previously, and further including aspects as in the remaining, dependent claims, including (but not limited to) the specific hydracid fluoride salt as in claims 34 and 35; and/or wherein the processing solution further includes a surfactant (see claim 36); and/or wherein the processing solution is ultrasonically vibrated in the cleaning step (see claim 37); and/or pH of the processing solution (see claim 40), or temperature of the processing solution during the processing (see claim 39); and/or wherein the heat treatment is performed without contacting the wafer with air as in claim 38; and/or wherein the heat treatment is performed in a mixed atmosphere of moisture and oxygen at a temperature of 800° to 900°C (see claim 41); and/or wherein the wafer is transferred immediately after the drying step to a chamber to perform the heat treatment, without exposure to the air (see claim 42).

The present invention is directed to a method of manufacturing a semiconductor integrated circuit device, including a cleaning process for a silicon wafer in cleaning the wafer having an insulating film (of a surface of silicon oxide in main part) thereon, prior to forming a gate oxide film of the device.

In manufacturing a large scale integrated circuit device using a wafer made of mono-crystalline silicon, a so-called RCA wafer cleaning technique has been used, as described in the paragraph bridging pages 1 and 2 of Applicant's specification.

There has been a desire to improve the RCA cleaning technique, and various proposals for improvement thereof have been made, as described on pages 2-4 of Applicant's specification. However, these proposed techniques have been insufficient, particularly in connection with forming an MOSFET which requires a thin gate oxide film of high quality. See the second full paragraph on page 4 of Applicant's specification. Note also the second full paragraph on page 4, and the paragraph bridging pages 4 and 5, of Applicant's specification, describing problems in connection with these proposed processing techniques. These techniques are particularly insufficient when processing the wafers in a sheet-by-sheet technique, wherein the processing is performed, e.g., at a higher rate.

Against this background, Applicant provides a method having especially advantageous effects for cleaning a semiconductor wafer, in processing prior to forming a gate oxide film of a semiconductor integrated circuit device. Applicant has found that by utilizing a processing solution containing hydrogen peroxide, hydric fluoride salt and water, the salt being included in an amount of about 0.1 to 3 mol/l, for cleaning the surface of the silicon wafer covered with an insulating film whose main surface is mainly formed of silicon oxide, under conditions where the insulating film (e.g., silicon oxide) is

etched but the silicon is not etched; and with this insulating film thereafter being removed to expose the surface of the silicon wafer; and the silicon wafer then being dried and then being subjected to a heat treatment to form the gate oxide film, the cleaning can be performed at relatively low temperatures, and the silicon oxide film is cleaned and etched without etching the silicon substrate, so that contamination of the substrate can be avoided. Moreover, through use of the processing solution of the present invention, in processing steps leading up to formation of the gate oxide film, with the insulating film being etched and the silicon wafer not being etched, the cleaning can be accomplished in a short time and at a low temperature, without deteriorating flatness of the wafer surface. Note, for example, the first full paragraph on page 6 of Applicant's specification.

Ohmi '060 discloses a cleaning method and a cleaning device which can remove foreign materials deposited on a substrate after removal of photoresist by plasma processing. See column 1, lines 6-10. This patent discloses that foreign materials can be removed under room temperature, by using a cleaning liquid which is a basic and water-soluble fluoride and an oxidizing agent, mixed in pure water. Note column 2, lines 20-29. See also column 2, lines 37-39 and 48-51; column 3, lines 42-47; and column 4, lines 45-50. This patent further discloses that by irradiating ultrasonic waves to the cleaning liquid or pure water, it is possible to improve the cleaning effect. Note the paragraph bridging columns 3 and 4 of this patent. This patent further discloses that the cleaning liquid can be applied not only to removal of photoresist, but also to removal of various types of high polymer organic coating films such as paint or adhesive, films of machine oil, as well as removal of surface surfactant or dye or the like. See column 8, lines 24-34. Note also the paragraph bridging columns 2 and 3;

and column 5, lines 7-10, of Ohmi '060. This patent, at the above-referred-to portion of column 8, specifically describes that the technique of Ohmi '060 is advantageously used for removing foreign materials deposited and remaining on the substrate even after a photoresist removal after ion injection and/or reactive ion etching processing used in a semiconductor production process or in a flat display panel production process. This patent discloses that the cleaning liquid has the characteristics that the liquid can etch silicon oxide film, silicon, Al or the like (see column 2, lines 37-39).

It is emphasized that the cleaning liquid in Ohmi '060 is described as having characteristics that the liquid can etch silicon. It is respectfully submitted that the teachings of this reference would have neither disclosed nor would have suggested, and in fact would have taught away from, cleaning as in the present claims, including, inter alia, wherein the cleaning is performed under conditions that the insulating film is etched but the silicon wafer is not etched. Particularly in view of advantages achieved according to the present invention, in increased flatness of the wafer because the wafer is not etched, clearly Ohmi '060 would have neither disclosed nor would have suggested the presently claimed invention, including various advantages thereof.

The contention by the Examiner on page 10 of the Office Action mailed June 4, 2003, that if the main surface is mainly formed of silicon oxide it would be clearly obvious that the processing solution etches the silicon oxide but does not etch the silicon wafer, is respectfully traversed. It is noted that, for example, films, even if covering a surface, could possibly have pathways to the substrate surface. Particularly in view of the known porosity of silicon oxide, it is respectfully submitted that the analysis by the Examiner that Ohmi '060 would etch the silicon oxide but does not etch the silicon wafer, without evidence in support thereof, is improper. To the contrary, it is

respectfully submitted that the present invention achieves advantages in increased wafer flatness due to use of the solution under conditions that the insulating film is etched but the silicon wafer is not etched; and neither the advantages, nor the processing achieving such advantages, would have been disclosed or suggested by the teachings of Ohmi '060, alone or in combination with the teachings of the other applied references.

Moreover, Applicant respectfully traverses the contention by the Examiner on page 3 of the Office Action mailed June 4, 2003, that in Ohmi '060 the processing solution includes HF and HF_2^- as etching seeds of silicon oxide. It is noted that at column 2, lines 32-34, Ohmi '060 discloses generation of HF_2^- ions used for etching the silicon oxide film, but does not specifically disclose generation of HF. It is respectfully submitted that Ohmi '060, either alone or in combination with the teachings of the other applied references, does not disclose, nor would have suggested, the process as in the present claims, including the recited cleaning, using the processing solution which, inter alia, also contains HF and HF_2^- as etching seeds of the silicon oxide, under conditions that the insulating film is etched but the silicon wafer is not etched.

It is emphasized that Ohmi '060 is concerned with a cleaning liquid and cleaning method removing organic materials, particularly removal of photoresist. It is respectfully submitted that this patent is primarily concerned with removal of photoresist in connection with ion injection or reactive ion etching processes, that is, after formation of the gate oxide and gate electrode. It is respectfully submitted that this patent does not disclose, nor would have suggested, the presently claimed method, including performance of the recited cleaning using the specified processing solution, prior to forming the gate oxide film, and advantages achieved.

It is again noted that according to the present invention, the processing solution is used under conditions where the silicon oxide is etched but the silicon wafer is not etched. This provides the additional advantage that while cleaning is achieved, a deterioration in flatness of the silicon surface of the silicon wafer can be avoided. Ohmi '060 does not disclose, nor would have suggested, this feature of the present invention, achieved by cleaning utilizing the recited processing solution, under the recited conditions, at the recited point in the sequence of steps as recited in the present claims.

It is emphasized that according to the present invention, the cleaning technique using the recited processing solution is a cleaning step prior to formation of the gate oxide film. Due to requirements of the gate oxide film, the present invention provides certain advantages, including wherein the surface of the silicon wafer is not etched. Therefore, it is possible to remove contamination without deterioration of the flatness of the silicon wafer surface, for example, so that a gate oxide film with a high quality can be advantageously formed according to the present invention.

In contrast, it is respectfully submitted that Ohmi '060 is concerned with a cleaning step after formation of the gate oxide film. It is respectfully submitted that the cleaning liquid of Ohmi '060 is directed to a cleaning after formation of the gate oxide and after removal of a photoresist mask, and would have neither taught nor would have suggested problems in connection with cleaning prior to forming the gate oxide film, as discussed in the foregoing, and overcoming such problems through use of the processing solution and conditions for cleaning as in the present invention.

Thus, it is respectfully submitted that the purpose and requirements with respect to cleaning prior to formation of the gate oxide film are different from those with respect

to cleaning after formation of the gate oxide film; and it is respectfully submitted that Ohmi '060 would have neither taught nor would have suggested the present invention, including cleaning using the recited processing solution as in the present claims, prior to formation of the gate oxide film, and advantages thereof.

Particularly in light of the unique problems arising in connection with forming gate oxide films after cleaning, which problems do not arise in cleaning after formation of the gate oxide film (and after formation of the gate electrode), and which problems are overcome by the present invention, as discussed previously, the contention by the Examiner concerning obviousness with respect to Ohmi '060 describing use of a processing solution in a cleaning process after formation of the gate oxide, is respectfully traversed.

It is respectfully submitted that, in the involved art, different cleaning solutions are used prior to, and subsequent to, forming the gate oxide film. In connection therewith, note Table 7 on page 254 of the publication Cleaning Technology for Silicon Wafer Surface (February 28, 1995), enclosed with the Submission Under 37 CFR § 1.114 (Amendment) filed May 16, 2003. This shows that different cleaning solutions are used in cleaning prior to and after formation of the gate oxide. It is respectfully submitted that this publication provides further evidence that one of ordinary skill in the art concerned with in Ohmi '060 would not have utilized the cleaning liquid described therein, in a cleaning step prior to formation of the gate oxide film.

It is respectfully submitted that the remaining references as applied by the Examiner in the Office Action mailed June 4, 2003, would not have rectified deficiencies of Ohmi '060, such that the presently claimed invention as a whole would have been obvious to one of ordinary skill in the art.

Wang discloses a method of manufacturing a semiconductor device including trench isolation. In a description of background art, this patent discloses a trench isolation technique including wherein, after the trench has been formed and filled, heating is utilized to densify the trench fill; and the remaining portion of the pad oxide layer is then removed with dilute hydrofluoric acid, followed by an industrial standard "RCA" clean, with a high quality gate oxide then being grown, followed by polysilicon deposition. Note, column 2, lines 9-41. This patent discloses a method of manufacturing a semiconductor device having an active region isolated by an isolation trench, including formation of a second oxide layer, as described in column 3, lines 32-63. This patent discloses that in accordance with the method described therein, a first sacrificial oxide layer is removed, by etching with dilute HF followed by a surface cleaning treatment commonly referred to as the "RCA" clean, with a mixture of hydrogen peroxide and ammonium hydroxide or a mixture of hydrogen peroxide and hydrogen chlorite. A second sacrificial oxide is removed, by etching employing a dilute HF dip followed by the standard "RCA" clean, exposing a fresh silicon surface, with a thin gate oxide layer being formed on this fresh silicon surface. Note from column 4, line 66 to column 5, line 28.

Initially, it is respectfully submitted that one of ordinary skill in the art concerned with in Ohmi '060 would not have looked to the teachings of Wang. In this regard, it is again respectfully submitted that Ohmi '060 is specifically directed to removing foreign materials deposited on a substrate after removal of photoresist by plasma processing. Wang does not refer to photoresists or, for that matter, to plasma processing for removing photoresists. Accordingly, it is respectfully submitted that one of ordinary skill in the art concerned with in Ohmi '060 would not have looked to the teachings of Wang.

In this regard, comments by the Examiner in the paragraph bridging pages 5 and 6 of the Office Action mailed June 4, 2003, are noted. The simple fact remains that Wang does not show photoresist use or plasma processing with respect to a photoresist, much less foreign materials deposited on a substrate after removal of photoresist by plasma processing. It is respectfully submitted that there is simply no basis for combining the teachings of Ohmi '060 and Wang, absent hindsight use of Applicant's disclosure which of course is improper under the guidelines of 35 USC §103.

It is emphasized that an object of the cleaning process in Ohmi '060 is to remove the foreign materials deposited on a substrate after removing a photoresist by plasma processing, and it is respectfully submitted that this cleaning process in Ohmi '060 is not intended for the precleaning performed prior to forming the gate oxide film, as in the present invention. Moreover, it is respectfully submitted that in the manufacturing process according to Wang, after forming the shallow trench isolation in a substrate a silicon oxide film is formed twice (pad oxide and second sacrificial oxide) on the surface of the substrate prior to forming the gate oxide film, and these silicon oxide films are removed by etching, and then a gate oxide film is formed. One object of Wang is to improve the edge shape of the shallow trench isolation. Moreover, the standard RCA cleaning solution is used as the etching solution cleaning solution in the manufacturing process in Wang. Especially since the manufacturing process of Wang does not consider removal of foreign materials at all, it is respectfully submitted that combination of the teachings of Ohmi '060 and of Wang, as applied by the Examiner, is clearly improper.

Moreover, it is noted that according to Wang, the sacrificial oxide layer is removed, and thereafter a surface cleaning treatment is performed. It is respectfully submitted that this disclosure, even in combination with the teachings of Ohmi '060, would have neither taught nor would have suggested, and would in fact have taught away from, a process wherein the cleaning of the surface using the processing solution is performed, and thereafter the insulating film is removed and thereafter (after drying) the gate oxide film is formed. That is, while Wang initially removes the pad oxide film and thereafter performs a cleaning, the present invention cleans and thereafter removes the insulating film. Clearly, the teachings of Wang, in combination with the teachings of Ohmi '060, would have taught away from the presently claimed subject matter, including wherein cleaning of the surface of the silicon wafer covered with the insulating film whose main surface is mainly formed of silicon oxide is performed using the recited processing solution, removing the insulating film after the cleaning thereby to expose the surface of the silicon wafer; and after such removing and after a drying treatment, subjecting the silicon wafer to a heat treatment thereby to form a gate oxide film over the silicon wafer, and advantages thereof as discussed in the foregoing. That is, it is emphasized that according to Wang the "RCA" treatment is performed after removal of the sacrificial oxide. Such procedure as in Wang would have taught away from the presently claimed process, including wherein the cleaning is performed and thereafter the insulating film is removed (that is, the cleaning is performed prior to removal of the insulating film).

The contention by the Examiner that Wang removes the insulating film after the cleaning, the Examiner referring to column 4, lines 31-33 and column 3, lines 50-52 of Wang, is noted. It is respectfully submitted, however, that at the cited portion of

column 4, the sequence of cleaning the main surface of debris and removal of the pad oxide is not set forth. In addition, the portion of column 3 of Wang, referred to by the Examiner, does not set forth a sequence. In any event, it is respectfully submitted that this teachings in Wang do not disclose, nor would have suggested, the presently claimed processing sequence.

The additional contention by the Examiner in Item 6 on page 12 of the Office Action mailed June 4, 2003, that Figs. 7-10 make clear that Ohmi '060 discloses use of the processing solution in a cleaning step before any layers (e.g., a gate oxide layer) are formed, is noted. It is noted that Figs. 7-10 of Ohmi, et al. are schematic, and focus on that aspect of Ohmi '060 of the photoresist mask layer and etching. See column 9, line 37 to column 10, line 8. Taking the teachings of Ohmi '060 as a whole, as required under 35 USC §103, it is respectfully submitted that this reference is directed to processing after forming the gate oxide film and gate electrode.

In any event, even assuming, arguendo, that the teachings of Ohmi '060 and of Wang were properly combinable, such combined teachings would have neither disclosed nor would have suggested the present invention, including cleaning the surface of the silicon wafer at an ordinary temperature with the recited processing solution, which also contains HF and HF₂⁻ as etching seeds of the silicon oxide, under conditions that the insulating film is etched but the silicon wafer is not etched, and advantages thereof as discussed in the foregoing.

Okutani discloses thin film-forming technology and etching technology in processing wafers used for semiconductor devices. The patent describes a method of producing semiconductor devices including dry and wet processing steps for the wafers, and a step for carrying wafers between the dry and wet processing steps, the dry and

wet processing steps and carrying step being continuously carried out in a predetermined atmosphere shutting off the open air. See column 2, lines 26-34. Note also, column 2, lines 42-54; and column 3, lines 57-64.

Even assuming, arguendo, that the teachings of Okutani were properly combinable with the teachings of Ohmi '060 and Wang, and the teachings of Ohmi '060 and Wang were properly combinable, such combined teachings would have neither disclosed nor would have suggested the cleaning, subsequent removing, subsequent drying, and subsequent gate oxide film forming steps, in the recited sequence as in the present claims, with the cleaning using the processing solution containing HF and HF₂⁻ as etching seeds for the silicon oxide, under conditions that the insulating film is etched but the silicon wafer is not etched, as recited in the present claims, and the advantages of this process as discussed previously.

Ohmi '835 discloses a surface treatment agent for use in fine surface treatment which is very effective for wet etching of silicon oxide film in the manufacturing process of semiconductor devices, as well as cleaning of fine-treated semiconductor devices. See column 1, lines 12-18. The surface treatment agent includes a mixed solution of fluoric acid, ammonium fluoride and water, the mixed solution containing specified amounts of hydrogen fluoride and ammonium fluoride. See column 3, lines 17-23.

Even assuming, arguendo, that the teachings of Ohmi '835 were properly combinable with the teachings of Ohmi '060, Wang, and Okutani, et al., as applied by the Examiner, it is respectfully submitted that the combined teachings of these references would have neither disclosed nor would have suggested the sequence of processing steps, including the cleaning step containing HF and HF₂⁻ as etching seeds for the silicon oxide, under conditions that the insulating film is etched but the silicon

wafer is not etched, the insulating film removing step, the drying step, and gate oxide film forming step, and advantages thereof, as discussed previously.

As applied by the Examiner, Wolf discloses thermal oxidation to produce SiO₂ films with controlled thickness and Si/SiO₂ interface properties.

Even assuming, arguendo, that the teachings of Wolf were properly combinable with the teachings of Ohmi '060, Wang and Okutani, et al., such combined teachings would have neither disclosed nor would have suggested the sequence of processing steps, including the cleaning step containing HF and HF₂⁻ as etching seeds for the silicon oxide, under conditions that the insulating film is etched but the silicon wafer is not etched, the insulating film removing step, the drying step and gate oxide film forming step, and advantages thereof, as discussed previously.

The contention by the Examiner in the first full paragraph on page 16 of the Office Action mailed June 4, 2003, that Ohmi '060 discloses a critical aspect of the current invention (i.e., the processing solution), is noted. However, as shown previously, Ohmi '060 does not disclose the processing solution of the present claims, or features thereof when used under conditions of the recited process. It is respectfully emphasized that the present claims are directed to a process having recited processing steps, including use of a processing solution having recited functions under conditions of processing, and also subjecting the silicon wafer to a heat treatment after removing the insulating film, thereby to form a gate oxide film over the silicon wafer. Properly construing the presently claimed subject matter as a whole, rather than merely focusing on components of the processing solution, it is respectfully submitted that the teachings of the applied references would have neither taught nor would have suggested the presently claimed invention.

Moreover, it is respectfully submitted that the Examiner has ignored unique problems arising in connection with cleaning prior to formation of the gate oxide film, as discussed previously and as described in Applicant's specification. Properly construed, it is respectfully submitted that, taking the present invention as a whole, the teachings of the applied prior art would have neither disclosed nor would have suggested the presently claimed subject matter.

In view of the foregoing comments and amendments, reconsideration and allowance of all claims presently in the application are respectfully requested.

To the extent necessary, Applicants petition for an extension of time under 37 CFR § 1.136. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to the Antonelli, Terry, Stout & Kraus, LLP Deposit Account No. 01-2135 (Docket No. 843.37558VX2) and please credit any excess fees to such Deposit Account.

Respectfully submitted,

ANTONELLI, TERRY, STOUT & KRAUS, LLP

By 
William I. Solomon
Reg. No. 28,565

WIS/sjg/dlt

1300 North Seventeenth Street, Suite 1800
Arlington, Virginia 22209
Telephone: (703) 312-6600
Facsimile: (703) 312-6666